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Combustion characteristics of chars from raw and torrefied willow

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There is much interest in co-firing biomass with coal in power plants. Torrefaction is a mild thermal pretreatment (T < 300 ˚C) that improves the milling and storage properties of biomass, making it more like coal, and thus more compatible with existing power plant equipment. We use non-isothermal thermogravimetric analysis to investigate the differences in oxidative reactivities between chars prepared from torrefied and raw willow. Both high- and low-heating-rate chars are investigated. High-heating-rate chars were prepared in a drop tube furnace at a temperature of 900 ˚C with a residence time of 2 s. Low-heating-rate chars were prepared in a crucible in a tube furnace, with a heating rate of 33 ˚C/min, a maximum temperature of 1000 ˚C, and a residence time of 1 hour at the maximum temperature. We find that torrefaction has a minimal impact on char reactivities for the low-heating-rate chars, while for the high-heating-rate case the chars prepared from raw willow are over twice as reactive as those prepared from torrefied willow.

1. Introduction

Pretreating biomass via torrefaction, a mild pyrolytic thermal treatment, provides many advantages for biomass combustion, especially when biomass is to be co-fired with pulverized coal in existing power plants. The increased energy density and brittleness and the lower water content of torrefied biomass give distinct advantages over raw biomass for transportation, storage, and milling [1,2]. Although a number of studies have focused on the effects of torrefaction on elemental composition and energy content of the solid residue, and milling properties, combustion properties of torrefied biomass have received relatively little attention [3]. Biomass combustion typically consists of partially overlapping release of water and volatiles, followed by a slower char burnout process that has an important impact on combustor sizing and efficiency [4]. In the current study, we investigate the oxidative reactivity of chars formed from torrefied willow, comparing them to those of chars from raw willow.

For both torrefied and raw biomass, we investigate reactivities of two different types of chars: high-heating-rate chars formed under conditions representative of pulverized coal furnaces, and low-heating-rate chars formed under conditions representative of moving grate combustors. Di Blasi [5] recently reviewed the reactivity of chars under both oxidation and gasification conditions and listed several factors resulting in increased char reactivity for chars formed with higher heating rates. Key among these was the effect on particle morphology of the pressurization occurring during high-heating-rate volatiles release. The deformation of biomass structures during rapid volatiles release typically leads to higher surface areas, especially in the macropore regime most important for oxidation reactivity. Torrefaction, which shifts volatiles release to the low-heating-rate torrefaction process, is expected to reduce this effect, and thus to lower the reactivity of high-heating-rate chars.

2. Experimental methods

Torrefaction. Willow chips were sieved to select those with their two smallest dimensions between 5.6 and 9.5 mm, and then dried at 110 °C for several hours. A packed bed of chips in a 6-cm-ID reactor was placed in the central zone of a temperature-programmed furnace and torrefied under a nitrogen flow. Batches of 70 g of willow were torrefied as follows: ramp at 5 °C/min from room temperature to 150 °C; hold at 150 °C for 45 min; ramp at 5 °C/min to desired end temperature (270 or 290 °C); hold at end temperature for either 41 or 38 minutes, giving a total time above 200 °C of approximately 60 minutes. Mass losses during torrefaction were 24% and 38% for the 270 and 290 °C cases, respectively.

Production of chars. Low-heating-rate chars were produced as follows: Torrefied or raw willow samples were milled in a Retsch PM 100 ball mill. Different milling regimens were used for the raw vs. the torrefied biomass. Raw biomass was processed at 450 rpm for one minute, 525 rpm for one minute, and 650 rpm for 45 seconds. Torrefied biomass was processed at 450 rpm for 30 seconds, followed by 650 rpm for 45 sec. In all cases, samples were then passed through a 1-mm sieve. Three one-gram samples of sieved material were placed in nickel crucibles, which were put inside a quartz reactor, which was placed in a furnace. Under a gentle nitrogen or argon flow, the reactor contents were heated at 33 °C/min from room temperature to 1000 °C, then held at 1000 °C for 60 minutes. The inert flow was maintained during the cooldown process. Mass losses during low-heating-rate char production were 82%, 76%, and 67%, respectively, for the raw willow, 270-°C torrefied willow, and 290-°C torrefied willow.

High-heating-rate chars were produced in nitrogen at 900 °C, in a drop-tube furnace with residence times of approximately 2 seconds and heating rates of over 500 °C/sec. [6].

Reactivity measurements; Non-isothermal kinetics were determined in a Netzsch STA 449C Jupiter simultaneous analyzer, by first heating the samples at 10 °C/min to a temperature of 100 °C; then maintaining the temperature at 100 °C for 20 min; and finally heating to 800 °C at 10 °C/min. A helium flow was maintained during the initial ramp and the first 15 minutes of the 100 °C period, after which a flow of 12.5% (molar) O_2 in He was substituted. Chars were freshly ground in an agate mortar but not sieved; sample mass was 10 ±1 mg. Good repeatability was obtained. The reactivity of the char was obtained from the mass measurements using equation (1), where the ash and moisture masses were obtained from the thermogravimetric measurements. Equation (1) as evaluated at selected temperatures between 400 and 600 °C, with mass measurements averaged over 5 °C intervals to reduce noise.

$$R = \left(-\frac{dm}{dt}\right)\left(\frac{1}{m - m_{ash} - m_{moisture}}\right) \quad (1)$$

3. Characteristics of biomass, torrefied biomass, and chars

Ultimate and proximate analyses of the willow and char samples were performed, as seen in Tables 1 and 2. The C, H, N and S contents were determined using a CE Intruments Flash EA 1112 Series elemental analyser. Proximate analyses were carried out according the European standards [8-10]. As seen in previous studies [1], both torrefaction and charring reduce H and O content and moisture and volatiles content. Figure 1 shows the particle size distribution of the raw and torrefied biomass after milling and immediately before charring, as obtained by sieving. Clearly, the two torrefied samples show very different size distributions than the raw willow sample, with much larger fractions of the mass in the small size ranges.

Table 1: Ultimate analysis of biomass, torrefied biomass, and char samples; mass percent on an as-received basis. LHR is low heating rate; HHR is high heating rate

Sample	C	H	N	S
Raw willow (RW)	48.28	5.86	0.32	0
Torrefied willow, 270 °C (TW-270)	54.29	5.57	0.38	0
Torrefied willow, 290 °C (TW-290)	58.38	5.55	0.38	0
LHR char from RW	87.65	0.81	0.48	0.02
LHR char from TW-270	85.46	0.62	0.39	0.04
LHR char from TW-290	89.89	0.61	0.40	0.02
HHR char from RW	73.77	1.20	0.56	0.02
HHR char from TW-270	86.56	1.20	0.52	0.01
HHR char from TW-290	85.85	1.20	0.55	0.03

Table 2: Proximate analysis of biomass and torrefied biomass samples; mass percent

Sample	Moisture content	Volatile content	Fixed carbon	Ash content
Raw willow (RW)	4.5	77.4	16.9	1.23
Torrefied willow, 270 °C (TW-270)	2.7	70.8	24.8	1.63
Torrefied willow, 290 °C (TW-290)	2.7	60.1	35.3	1.91

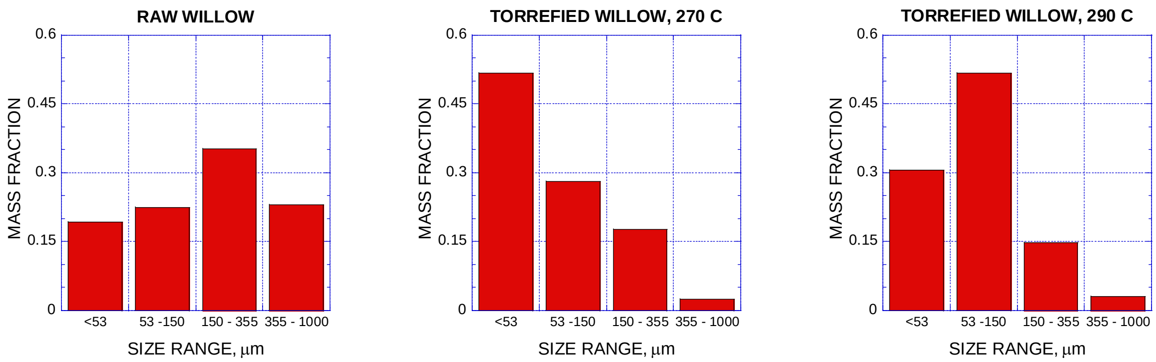

Figure 1: Particle size distribution before charring

4. Reactivity Results and Discussion

Reactivity results over the temperature range 400-600 °C are shown in Figure 2. High- and low-heating rate chars show distinctly different effects of torrefaction, and these differences are consistent across the entire range of temperatures, i.e. for conversions between about 20% and 90%. As indicated in the literature [5,11], higher-heating-rate chars are more reactive than low-heating rate chars from the same solid fuel. The effect of torrefaction is very different for the two charring methods. When chars are formed with low heating rates, torrefaction has little or no effect on char reactivity, except possibly at temperatures above 525 °C. With high-heating-rate char formation, however, torrefaction has a dramatic effect. Little difference is observed between the chars from torrefied samples prepared at two different temperatures, but the two torrefied samples produce chars with dramatically lower reactivities than the char from the raw willow. This result is consistent with Bridgeman's findings for high-heating-rate chars produced in a pyroprobe [12]. The torrefied and non-torrefied chars have similar apparent activation energies, but differ in reactivity by more than a factor of two. All these findings support the notion that the volatiles release during char formation at high heating rate increases reactivity, probably through changes in the structure and pore distribution of the biomass [5]. It is highly plausible that torrefaction reduces the intensity of that volatiles release, resulting in lower reactivity.

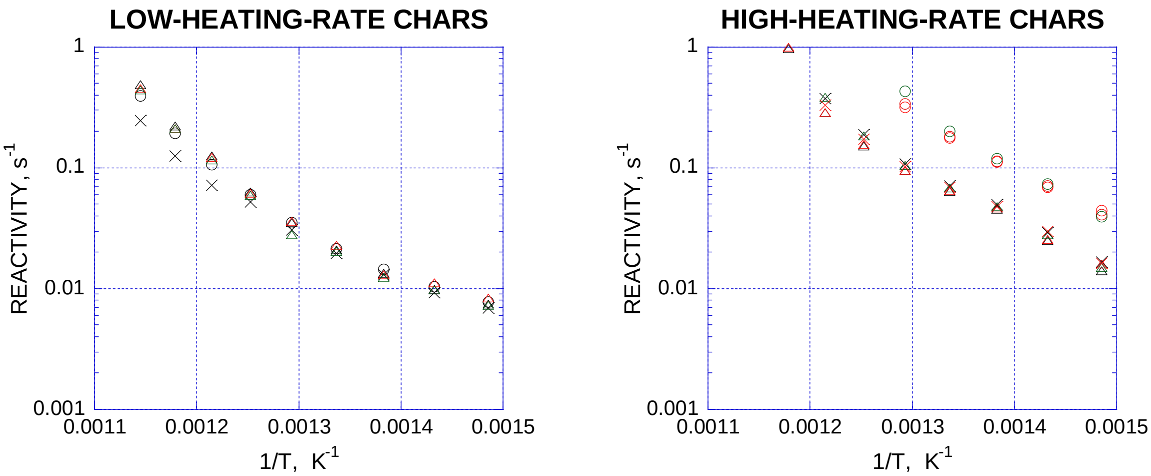

Figure 2: Reactivity, R.

Circles: raw willow; triangles: torrefied willow, 270 °C; x's: torrefied willow, 290 °C. Different colors correspond to different runs.

5. Summary and conclusions

Chars from torrefied biomass are less than half as reactive as those from raw biomass, when prepared under high heating rates. Low-heating-rate chars are not much affected by torrefaction. These results are consistent with the literature observation that volatiles release alters biomass morphology in a way that increases reactivity. Even though chars from torrefied biomass are less reactive than those from raw biomass, they are still more reactive than typical coal chars [7]. Thus co-firing of torrefied biomass should not require resizing of combustion chambers for adequate burnout.

Acknowledgments

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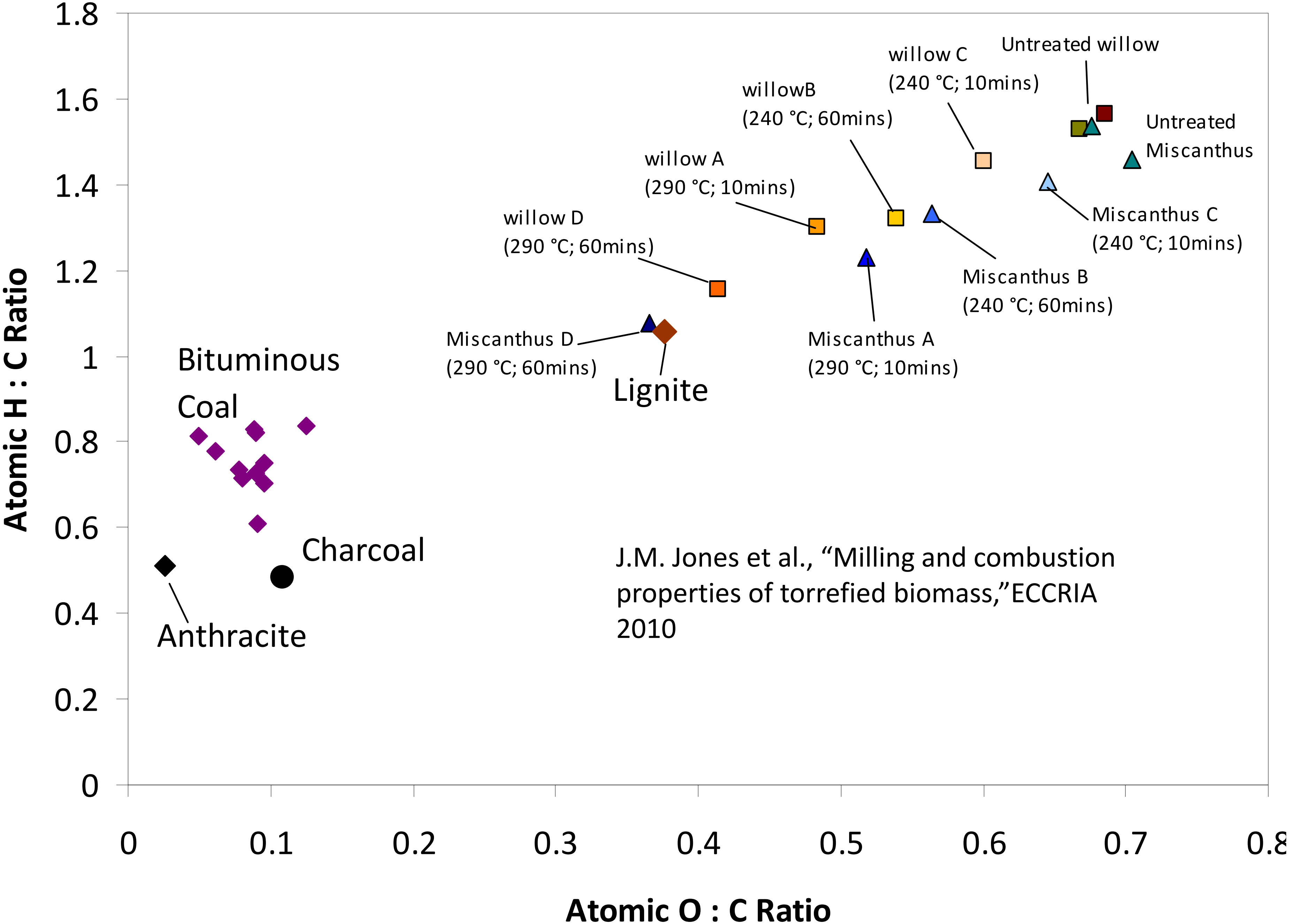
What is torrefaction??

- A mild thermal pretreatment for biomass fuels, similar to coffee roasting.

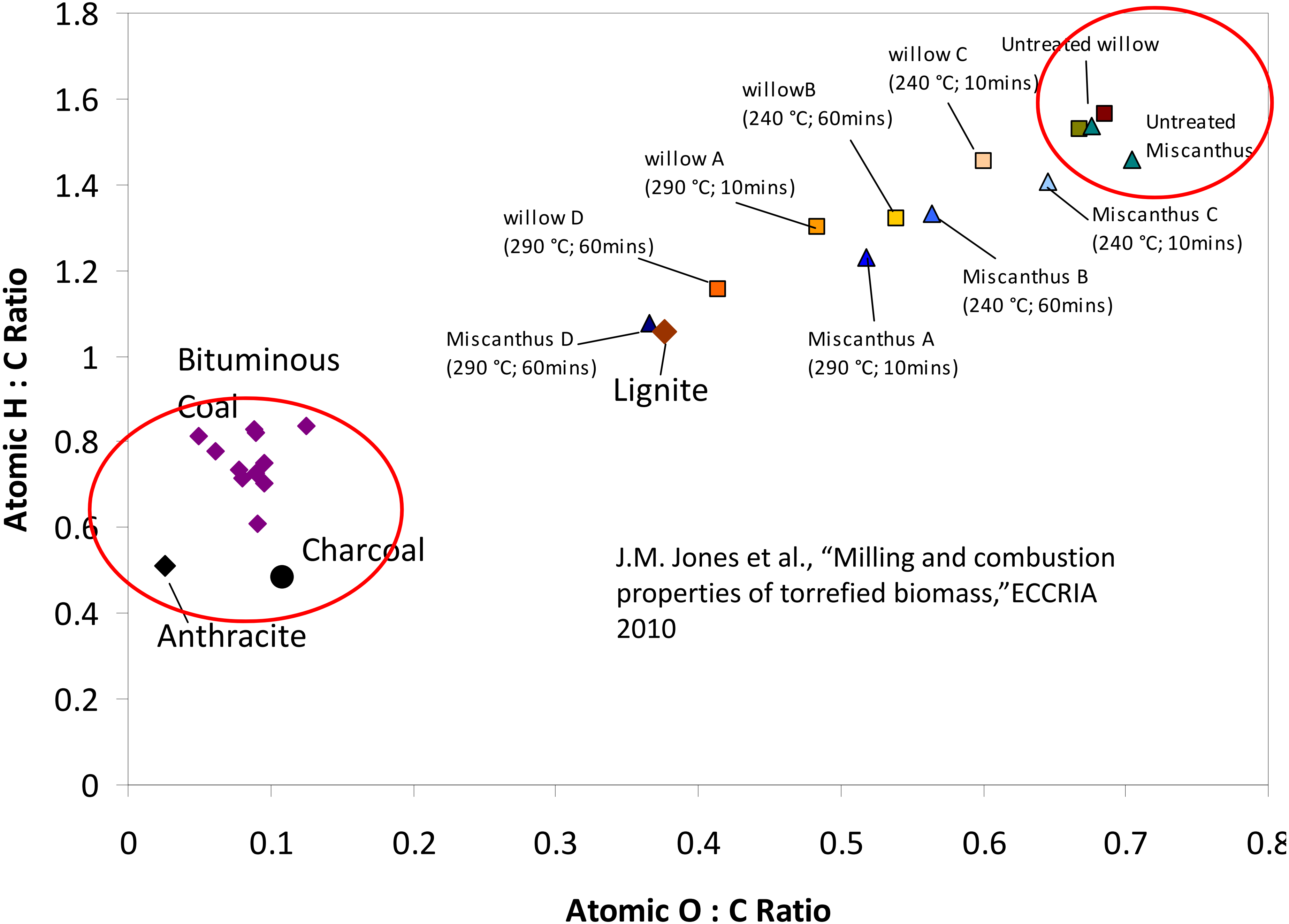
http://eatathomecooks.com/2009/07/home-roasted-coffee-beans.html

Late latin *torrere* = to parch, to roast

Van Krevelen diagram - Changes upon torrefaction



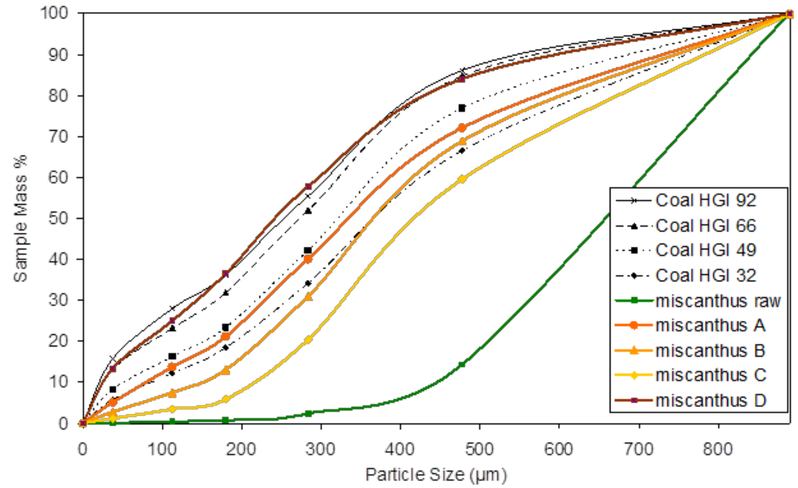
Van Krevelen diagram - Changes upon torrefaction



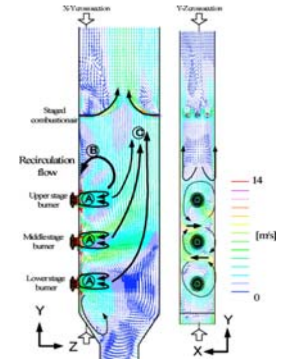
Advantages of torrefaction

- 10% higher energy density (mass basis) → Reduced transportation costs
- Hydrophobicity → storage advantages
- Improved grinding characteristics → co-grind with coal
- Loss of approximately 10% of fuel energy compensated by reduced grinding and transportation costs.

J.M. Jones et al.,
ECCRIA 2010



Char reactivity



N. Hashimoto et al. *Energy Fuels*, 2007 21:1950-1958.

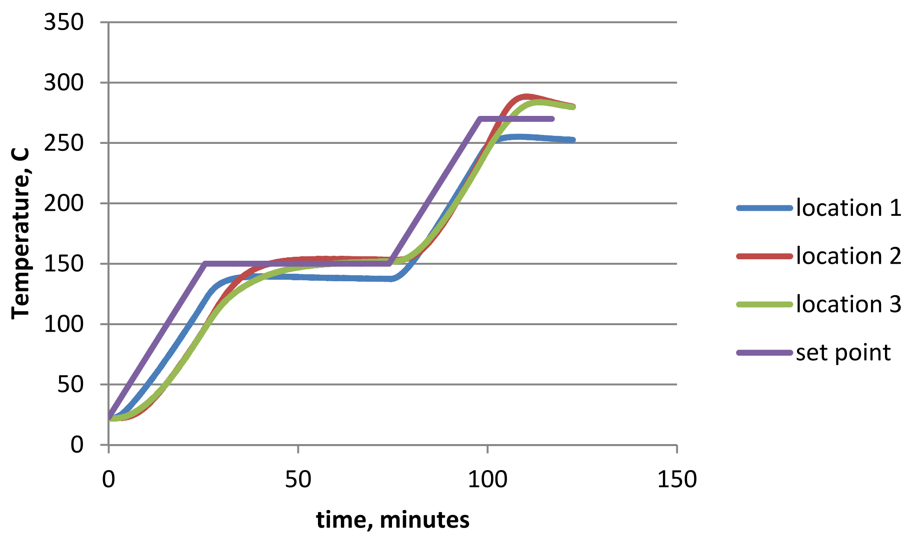
- 2 stages in solid fuel combustion:
  - Volatiles release/char formation
  - Char burnout: key in sizing of combustion equipment.
- Previous literature: fast-pyrolysis chars are more reactive than slow-pyrolysis chars; this difference is attributed to formation of macro- and meso-pores during rapid volatiles release (e.g. C. Di Blasi, *PECS* 35 (2009) 121-140).

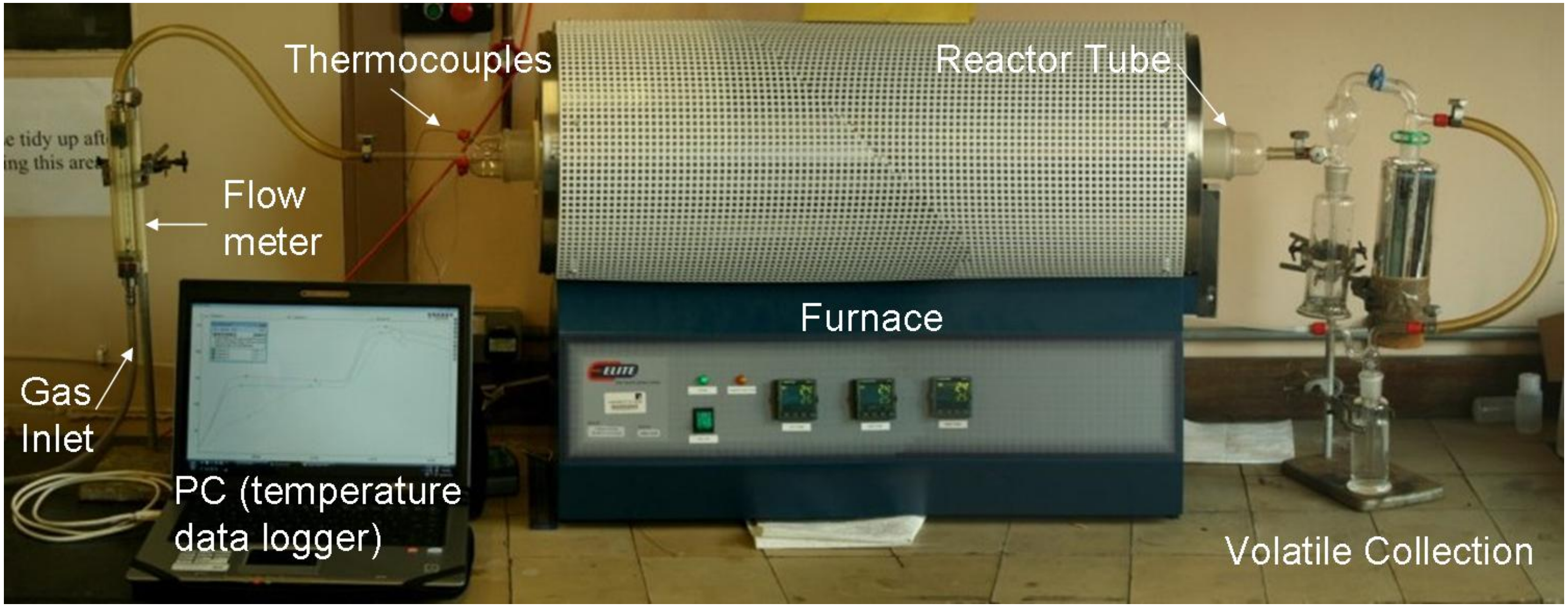
Expected effect of torrefaction on char reactivity

- *Hypothesis: Lower volatiles content of torrefied biomass will lead to less deformation during char formation – thus torrefied chars' reactivity will depend less strongly on charring conditions.*
- *Approach:*
  - *Feedstocks: torrefied and raw biomass.*
  - *Prepare series of chars with different heating rates.*
  - *Compare combustion reactivity of chars.*

Torrefaction process

- T_{max}= 270 °C, 290 °C,
- 60 min spent above 200 °C, and
- d = < 9.5 mm, > 5.6 mm, Willow





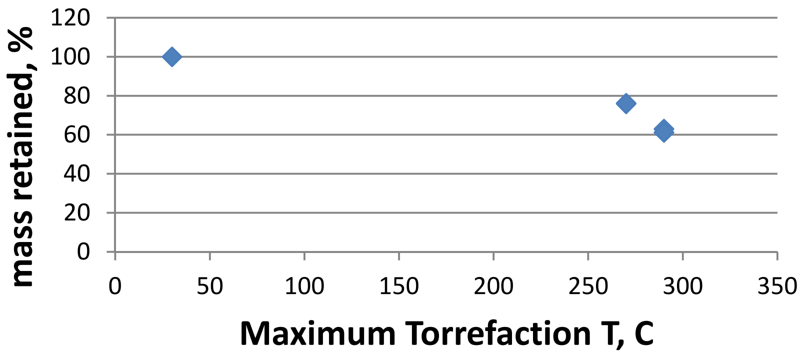
Willow chips in furnace

Raw willow

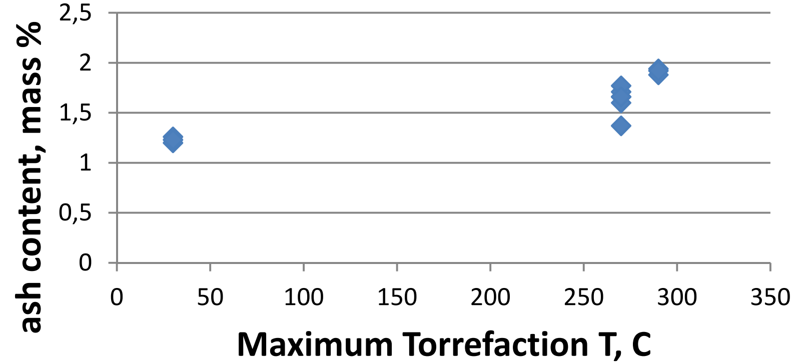
Torrefied willow

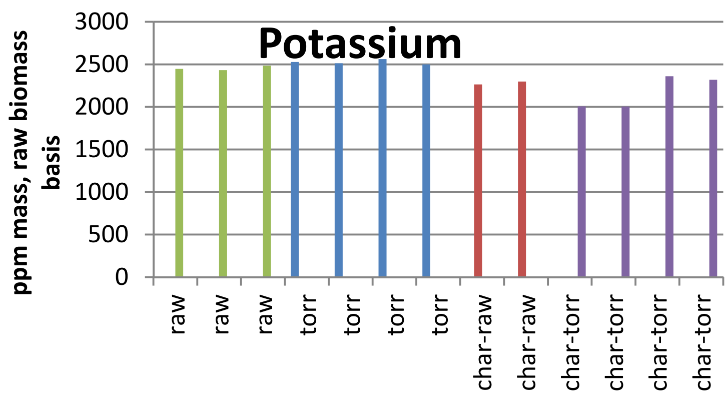
Mass and composition changes during torrefaction

MASS LOSS

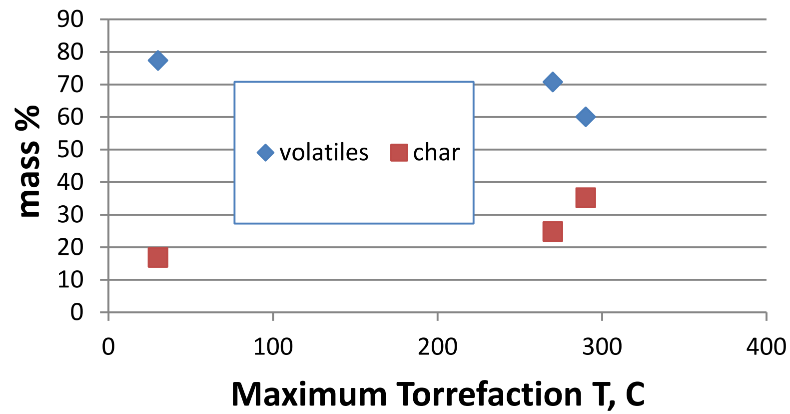


ASH CONTENT





MINERAL CONTENT



PROXIMATE ANALYSIS

Proximate analysis, mass percent

Sample	Moisture content	Volatile content	Fixed carbon	Ash content
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Torrefied willow, 270 °C (TW-270)	2.7	70.8	24.8	1.63
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Ultimate analysis; mass percent on an as-received basis.

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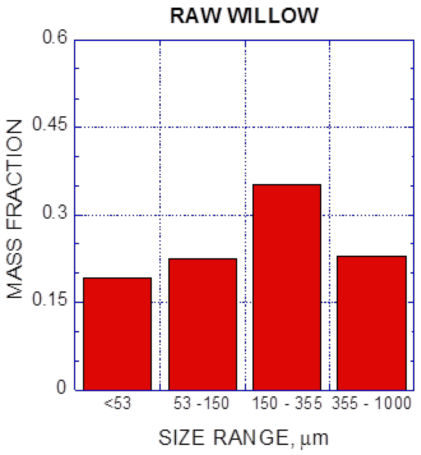
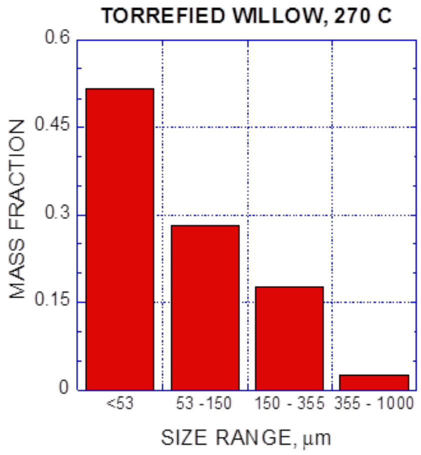
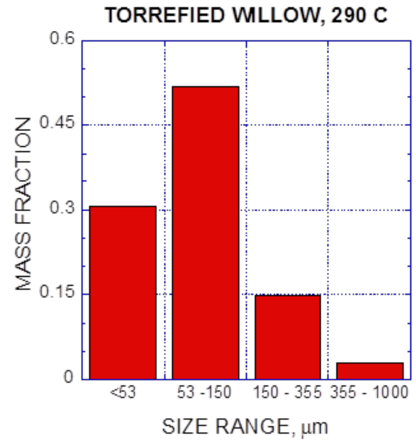
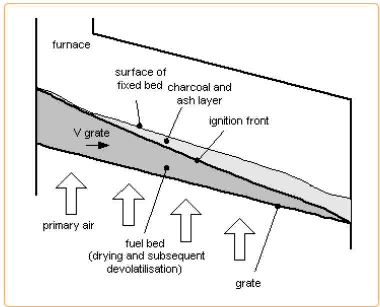
Particle size distributions, after ball milling



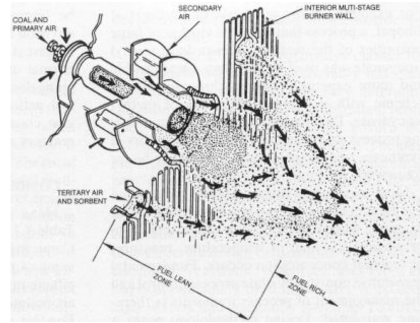




Methods of producing char from milled willow and milled torrefied willow



IEA Bioenergy task force 32

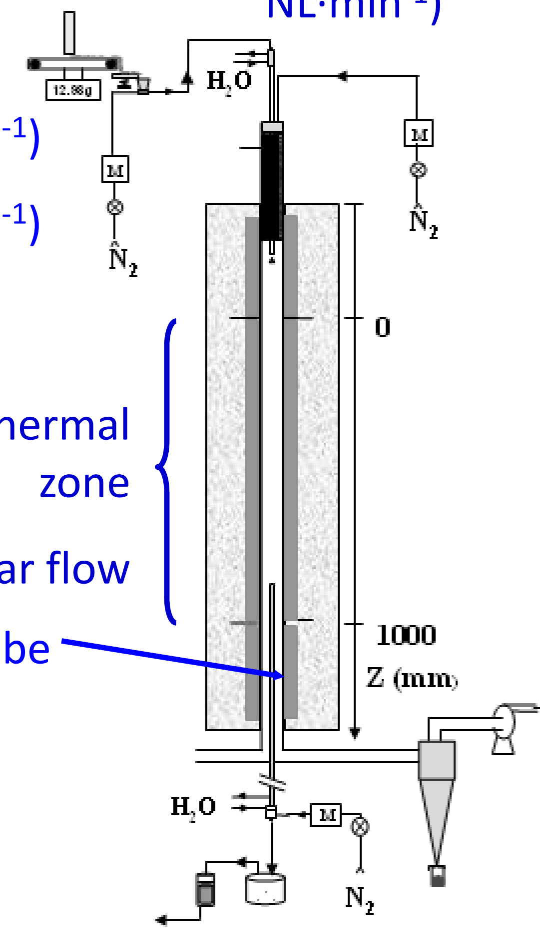


http://navier.engr.colostate.edu/whatische/ChEL02Body.html

Method name	Heating rate, C/min	Maximum T, C	Residence time at max T, min	apparatus
SLOW-1000	33	1000	60	Open crucible inside temperature-programmed tube furnace; N_2 or Ar flow
SLOW-850	33	850	30	Open crucible inside temperature-programmed tube furnace; N_2 or Ar flow
INT	~200	900	~3	Crucible with lid, inserted into hot furnace
FAST	>100,000	900	0.03	Entrained flow reactor; N_2 flow

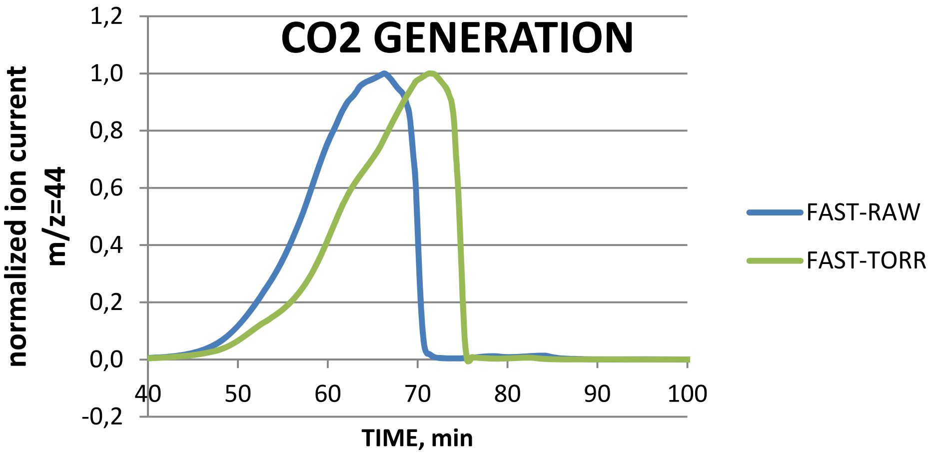
Drop tube entrained flow reactor, Ecole des Mines d’Albi

Temperature (°C)	900
Pressure (bar)	1 (open reactor)
Reaction zone length (m)	0.9
Solid residence time (s)	~2 s

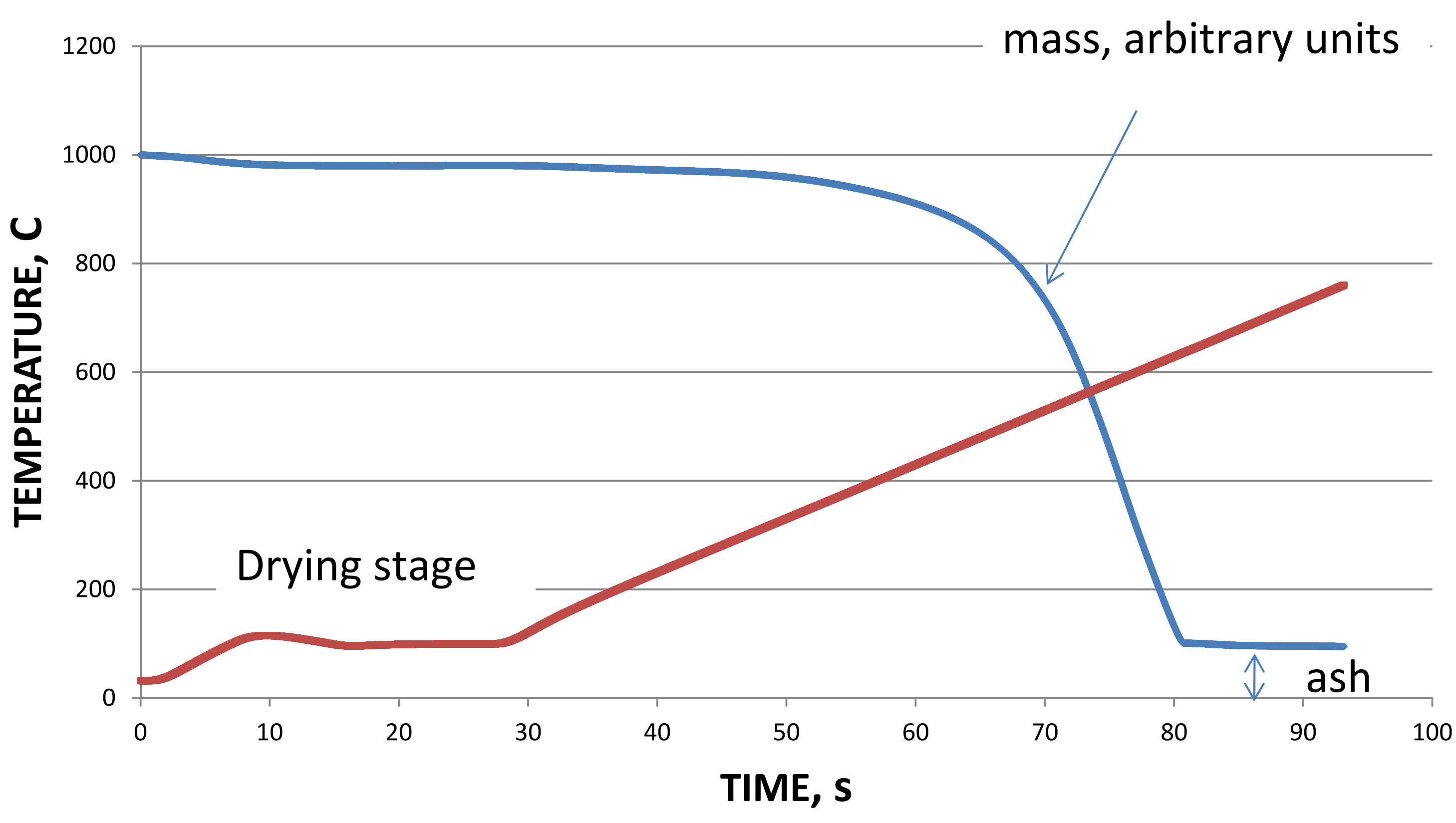


Char oxidation kinetics: method

- 10 mg of freshly ground char in crucible is heated under O_2/He in a thermogravimetric analyzer
- Measure mass as fn of time; correct for buoyancy
- Measure mass spectra of products (electron ionization)
- Express mass evolution in terms of first order reaction rate (assuming kinetic control)



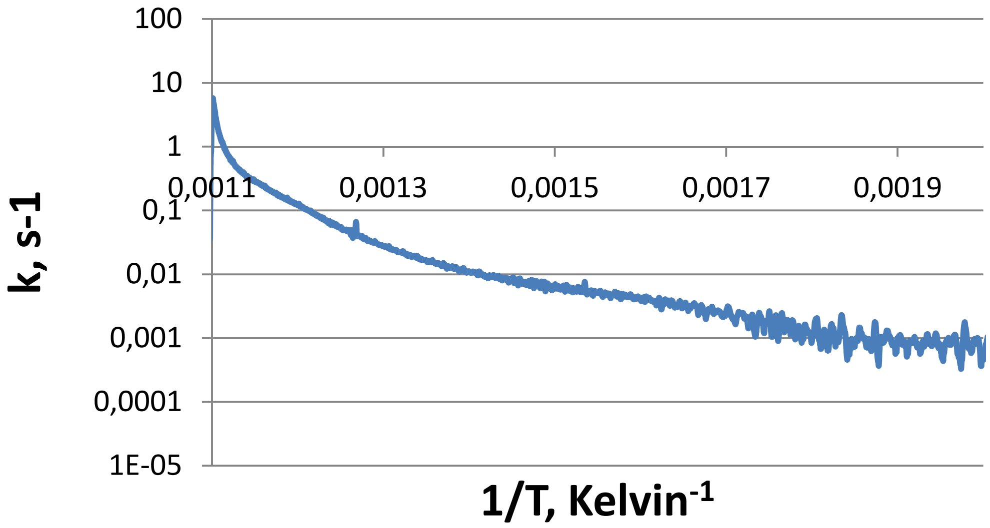
Temperature profile and mass evolution



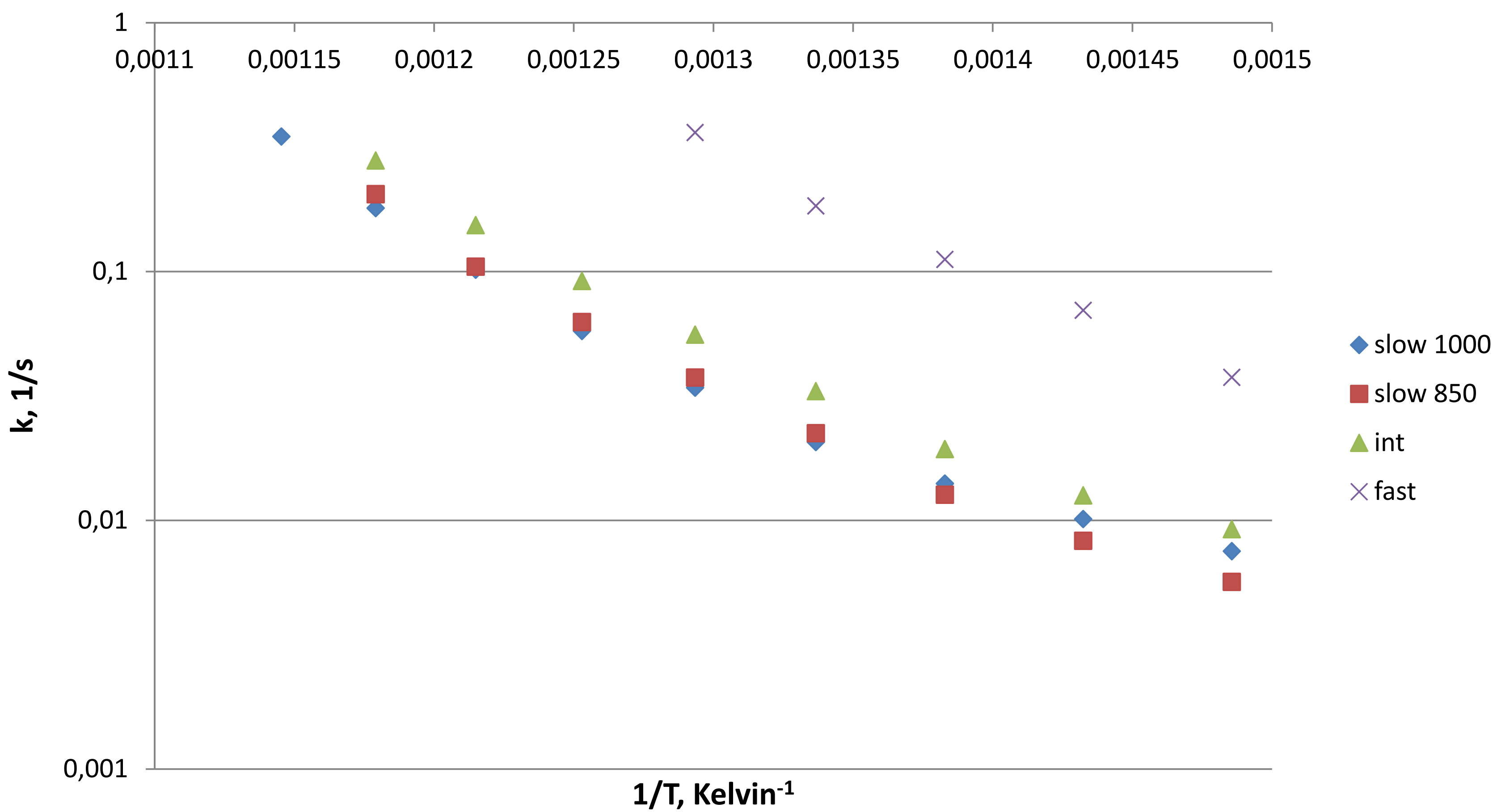
First order kinetics

- $dm/dt = -k\,(m - m_\infty)$
- find k(T) from m(t) and T(t)
- For Arrhenius kinetics: $k = A \exp(-Ea/(RT))$ →

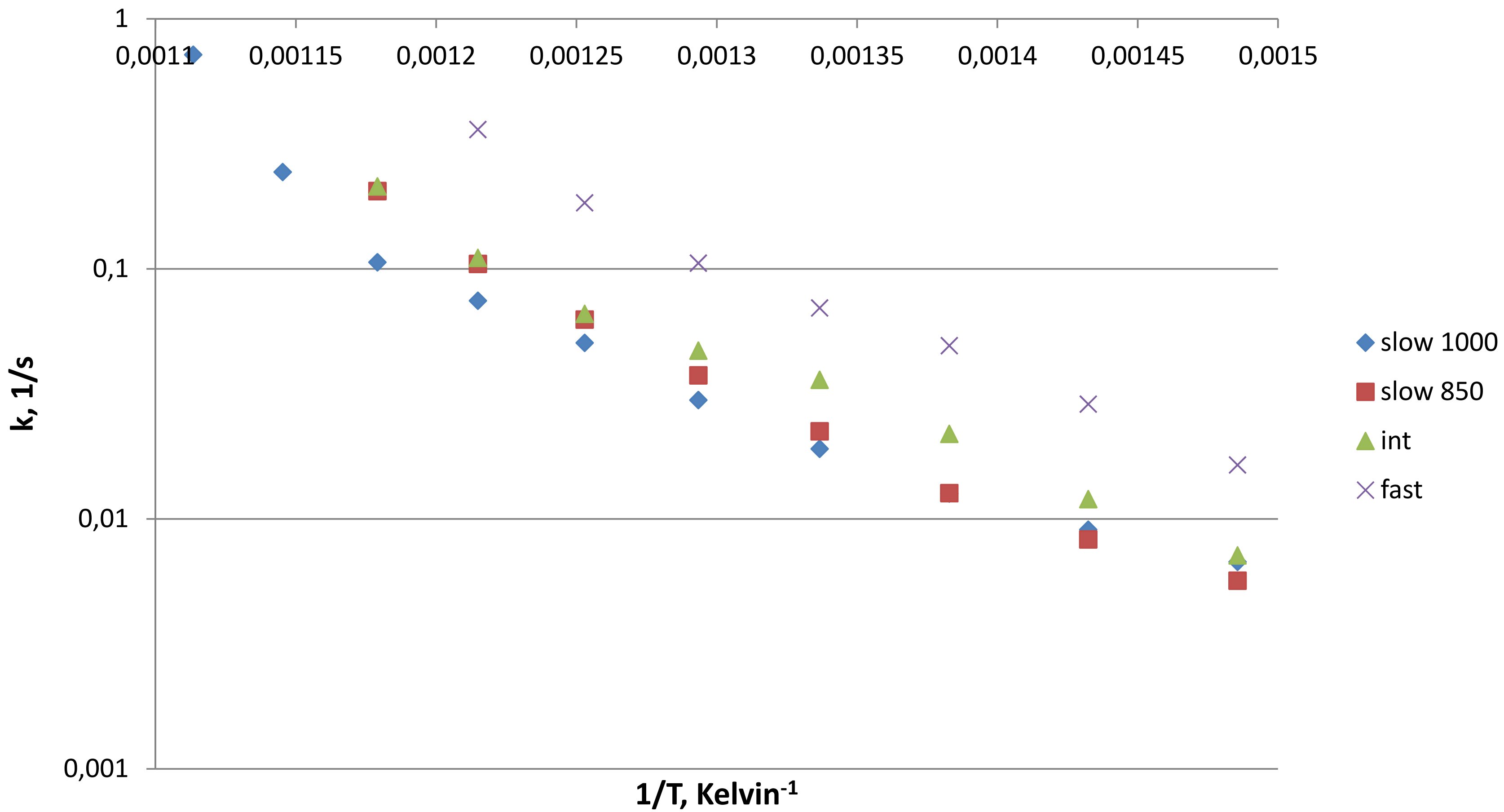
  ln(k) vs 1/T is a straight line



Reactivities of chars prepared from raw willow with different methods

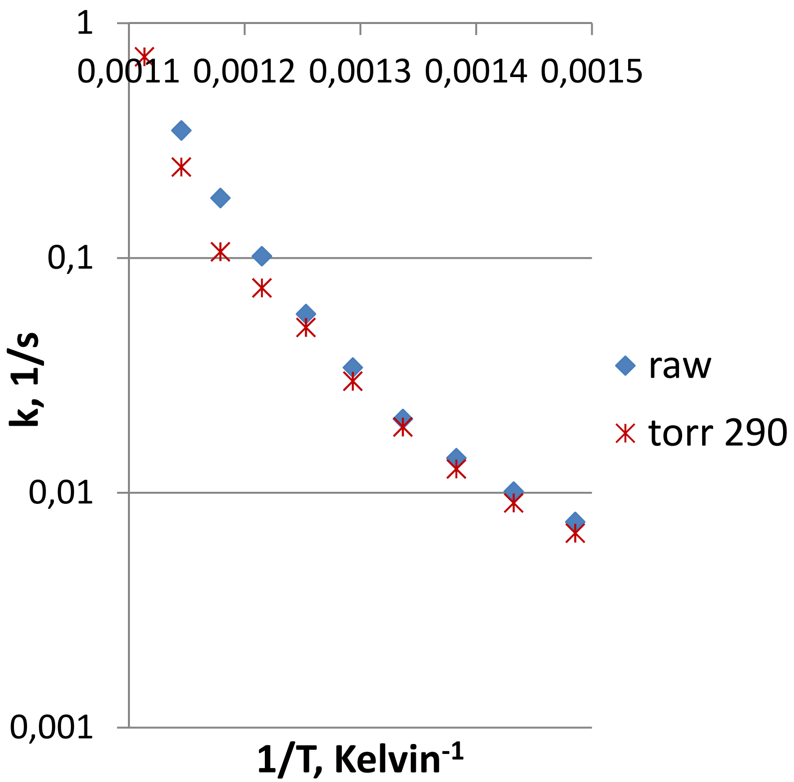


Reactivities of chars from torref. willow (290 C) with different charring methods

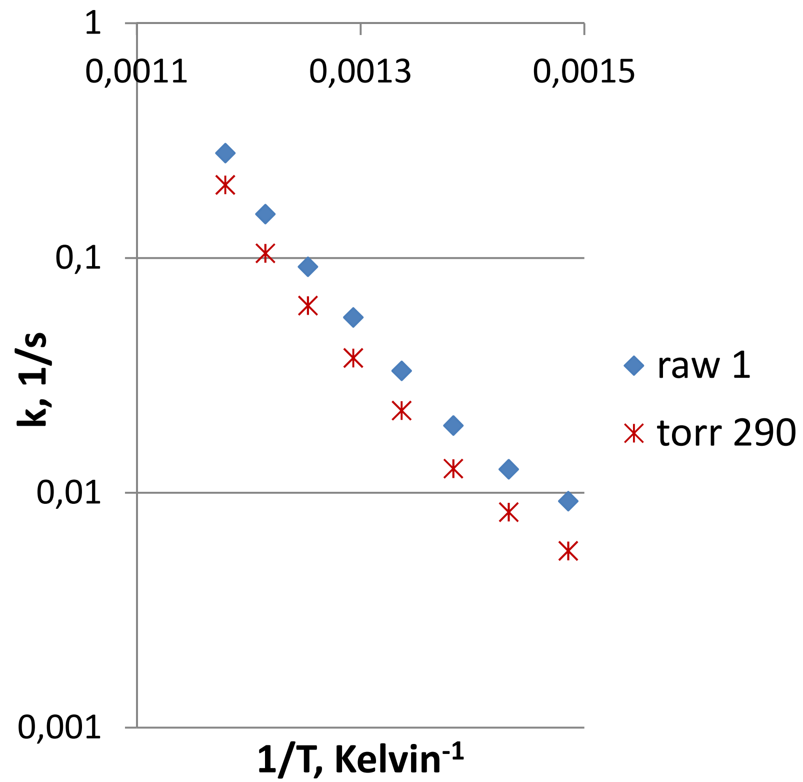


Comparison of chars from torrefied vs. raw biomass

CHAR SLOW-1000

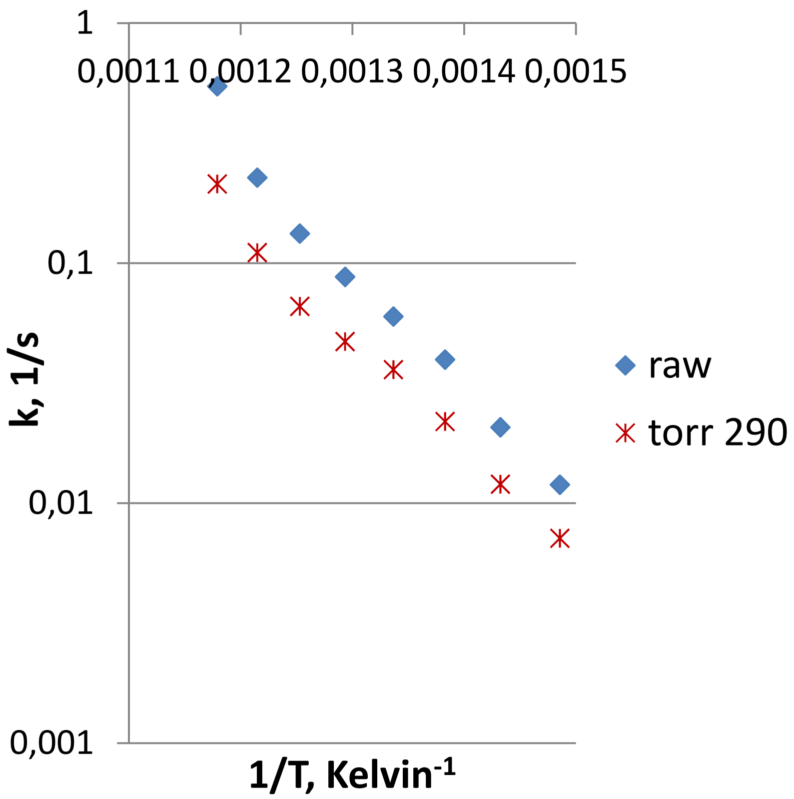


CHAR SLOW-850

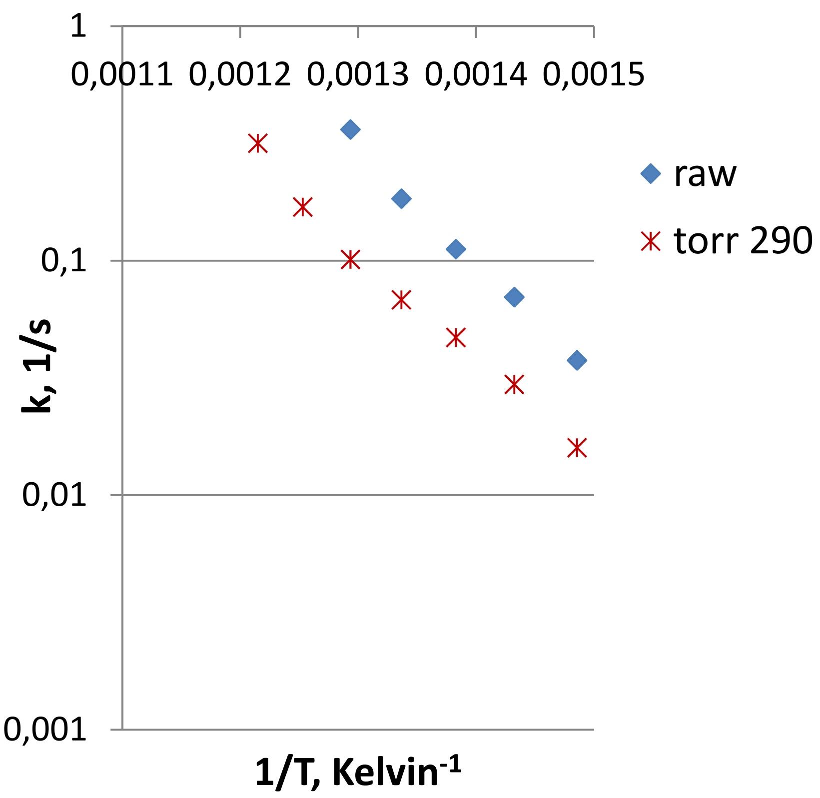


Comparison of chars from torrefied vs. raw biomass

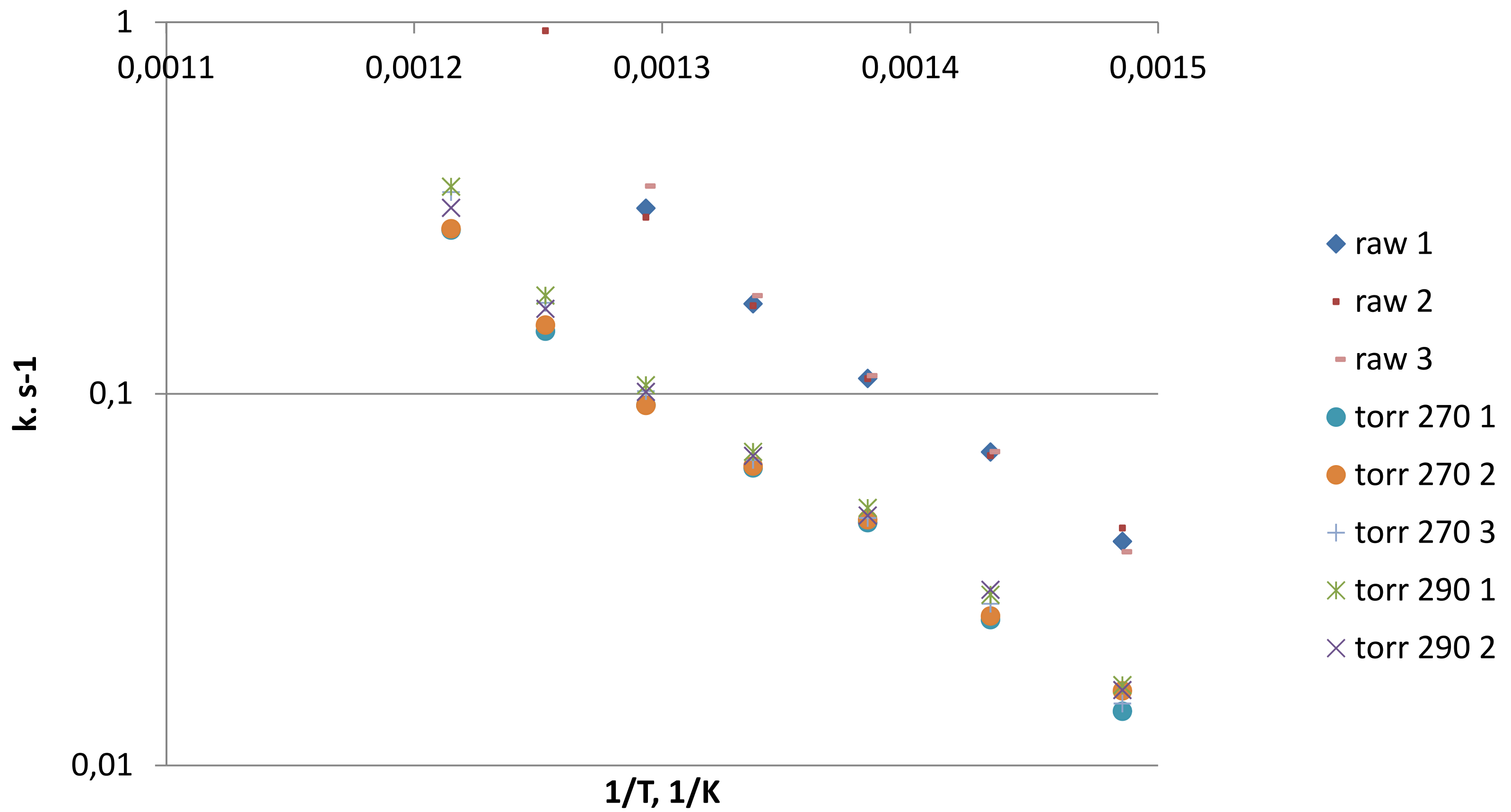
CHAR INT



CHAR FAST



Impact of torrefaction temperature on char reactivity, high heating rate chars



Summary

- Qualitative effects of char production conditions are similar for raw and torrefied biomass, but impact is smaller for torrefied biomass.
- For fast pyrolysis, raw biomass produces chars that are more than 2-8 times as reactive as chars from torrefied biomass. Harsh, slow charring conditions tend to erase the reactivity differences between torrefied and raw biomass.
- Details of torrefaction process have little effect on reactivity.
- Torrefied biomass chars are still more reactive than typical coal chars.

Future work

- Steam gasification reactivity (CEA, Grenoble)
- Scanning electron microscope photography for qualitative information about char morphology.

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